JOC The Journal of Organic Chemistry

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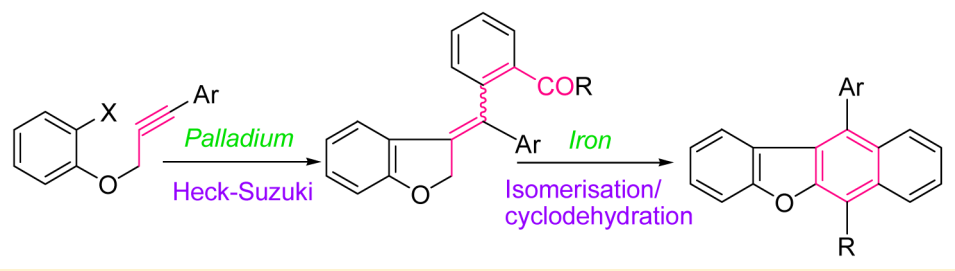
Synthesis of Fused Dibenzofuran Derivatives via Palladium-Catalyzed Domino C–C Bond Formation and Iron-Catalyzed Cycloisomerization/Aromatization

Kartick Paul, Swapnadeep Jalal, Sandip Kundal, and Umasish Jana*

Department of Chemistry, Jadavpur University, Kolkata 700 032, West Bengal, India

Supporting Information



ABSTRACT: A range of tetracyclic dibenzofuran derivatives bearing a variety of functional groups was readily synthesized via a two-stage domino strategy starting from propargyl ethers of 2-halo phenol derivatives. The first stage in the strategy involves Pd(0)-catalyzed domino intramolecular carbopalladation/Suzuki coupling via 5-*exo*-*dig* cyclization onto the alkyne, leading to 3-methylene-2,3-dihydrobenzofuran derivatives. In the second stage of the domino strategy, an iron(III)-catalyzed cycloisomerization and aromatization reaction produces tetracyclic benzofuran derivatives. This two-step sequence provides efficient access to diversely substituted polycyclic dibenzofuran derivatives in high yields and in an atom-efficient and environmentally friendly manner. Moreover, this strategy was also successfully used for the synthesis of a naturally occurring tetracyclic dibenzofuran, *β*-brazan.

INTRODUCTION

Polycyclic oxygen heterocycles constitute an important class of fused heterocycles found in numerous natural products and possess interesting biological properties. In particular, dibenzofuran derivatives are an important class of heterocyclic compounds that have attracted much interest over the years because of their occurrence in many natural products,[1] in materials science,[2] and in pharmaceutically active compounds, where they exhibit anticancer, antibacterial, antiallergy, antimalarial, and anti-inflammatory activities.[3] Because of their broad range of biological activities and interesting pharmaceutical properties, many synthetic routes have been developed to access dibenzofuran derivatives.[4] In addition, dibenzofurans embedded in tetracyclic structures have also been found in many biologically active natural products and pharmaceutically active agents (Figure 1). For example, tetracyclic *β*-brazan **1a** was isolated from the bark of *Caesalpinia echinata* Lamarck (Brazilwood).[5a] It has also been reported that tetracyclic dibenzofuran derivatives exhibit selective PTPase inhibition that allows them to function as oral antidiabetic agents.[5b] Compound **1a** and its derivatives can also be oxidized to benzo[*b*]naphtha[2,3-*d*]furan-6,11-dione **1b**, which exhibits promising anticancer and anticoccidial W5599A activities.[5c,d] The tetracyclic structure balsaminone **A** (**1c**) was isolated from the pericarp of fruit of *Impatiens balsamina* L; this compound has significant antipruritic activity.[5e] Similarly, benzofurobenzofuran derivative **1d** exhibits strong potent antitubercular and antimycobacterial activities.[5f] Notably, benzofuroindole framework **1e** is highly efficient in the treatment of sexual hormone disorders and degenerative brain diseases and elicits antitumor activity.[5g,h] Moreover, derivatives benzofuro[2,3-*b*]quinoline **1f** and benzofuro[2,3-*b*]pyridine **1g** have been reported to be an antituberculosis agent and an inhibitor of CDK1, CDK5/p25, and GSK-3b, respectively.[5i]

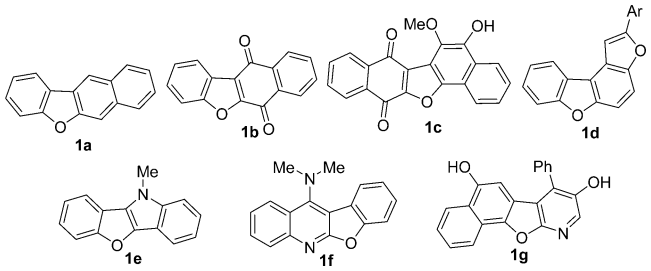


Figure 1. Fused dibenzofuran derivatives in natural and medicinal compounds.

However, a literature search revealed that a few methods have been developed for the synthesis of tetracyclic

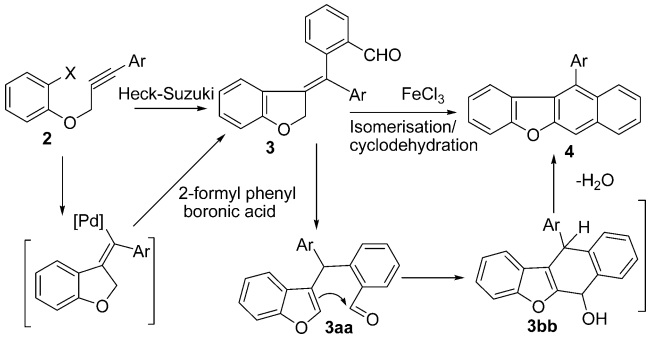
Received: November 25, 2015
Published: January 5, 2016

DOI: 10.1021/acs.joc.5b02637
J. Org. Chem. 2016, 81, 1164–1174

dibenzofuran derivatives.[4,5b,6] Moreover, the described protocols are subject to some limitations, such as the nonavailability of starting materials, lack of generality, multistep operation, harsh reaction conditions, low chemical yields, and unsatisfactory scope and efficiency. Owing to their important biological activities, a reliable synthetic method for this class of compounds in an efficient and atom-economical manner is required to further develop them for use in the area of drug discovery and the development of new materials.

In recent years, a significant challenge for the synthesis of polycyclic molecules has been the development of a transition metal-catalyzed domino process that allows the construction of complex molecules starting from simple substrates in a few steps. In this context, palladium-catalyzed domino reactions have proved to be extremely powerful tools for the construction of polycyclic compounds.[7] In a continuation of our investigation into the synthesis of polycyclic heterocycles,[8] we recently disclosed palladium-catalyzed domino carbopalladation/Suzuki reactions and an iron(III)-mediated cycloisomerization/aromatization reaction for the simple synthesis of fused carbazoles, C-3 substituted indoles, and benzofuran derivatives.[9] This strategy was found to be very efficient, atom-economical, and environmentally friendly. Encouraged by these results, herein, we report a simple, convenient, and highly efficient two-stage domino approach for the synthesis of diverse tetracyclic dibenzofuran derivatives starting from propargyl ethers of *o*-halo-phenol derivatives as the starting materials. Our strategy is depicted in Scheme 1. The first stage of this domino

Scheme 1. Strategy To Construct Substituted Tetracyclic Dibenzofurans



strategy involves intramolecular carbopalladation/Suzuki coupling of **2** to produce 3-methylene-2,3-dihydrobenzofuran derivative **3**. The reaction proceeds through an intramolecular *syn*-carbopalladation onto the alkyne via a 5-*exo*-*dig* process, producing a σ-alkylpalladium(II) intermediate. Subsequent intermolecular Suzuki coupling with 2-formyl phenylboronic acid derivatives gives bicyclic product **3** in a stereoselective manner. In the second stage of this domino strategy, compound **3** undergoes Lewis acid-mediated isomerization to **3aa**, followed by cyclization and aromatization reactions to generate tetracyclic dibenzofuran **4**. Significantly, the present method furnished a wide range of functionalized tetracyclic benzofuran derivatives with excellent regioselectivity.

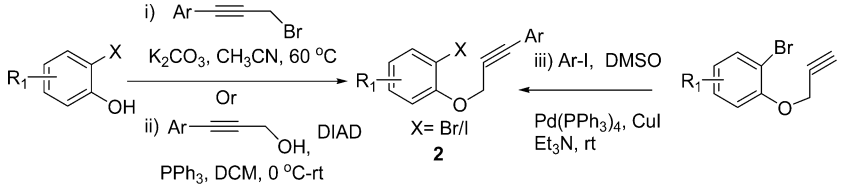
RESULTS AND DISCUSSION

First, we prepared a series of 2-halo propargyl ethers derivatives **2** through two different routes (Scheme 2): (a) reaction of 2-halo phenols and aryl propargyl bromide in the presence of K_2CO_3 in CH_3CN or Mitsunobu reaction of 2-halo phenols with propargyl alcohols or (b) selective Sonogashira cross-coupling of 1-bromo-(2-prop-2-ynyloxy)benzene derivatives with a variety of aryl iodides (Scheme 2). We have found both methods to be reliable and reproducible for reactions on both small and large scales and to give high yields.

After obtaining a series of 2-halopropargyl ethers, we investigated the synthesis of a large array of tetracyclic dibenzofuran derivatives via our previously developed two-step method, as described in Scheme 3.[9] First, we carried out a domino Heck–Suzuki coupling between **2a** and 2-formyl phenylboronic acid to prepare intermediate compound **3a** according to our previously developed method using 5 mol % of $Pd(OAc)_2$, 10 mol % of tricyclohexylphosphine (PCy_3) as ligand, and 2.5 M K_2CO_3 in combination with ethanol and toluene at 60 °C. Under these conditions, 3-methylene-2,3-dihydrobenzofuran **3a** was obtained in 90% yield. In the next step, compound **3a** was dissolved in 1,2-dichloroethane, to which $FeCl_3$ (10 mol %) was added at room temperature. It was observed that the final isomerization/cyclization and aromatization process took place efficiently and afforded tetracyclic dibenzofuran **4a** in 95% yield within a short period of time at room temperature.

Next, we sought to prepare a series of substrates (**3b–3l**) through Heck–Suzuki coupling with 2-formyl phenylboronic acid under the above described conditions. We noticed that in many cases a mixture of nonseparable isomers was isolated. To avoid the separation process, we decided to couple the above described two-step domino strategies in one pot. Unfortunately, after completion of Heck–Suzuki coupling, we observed that no reaction took place when we added iron(III)-salt or any other Lewis or Brønsted acid directly to the reaction mixture. To our delight, when crude intermediate **3a** (just after extraction with ethyl acetate and removal of solvent) was subjected to a second round of domino reactions without purification in the presence of anhydrous $FeCl_3$ (10 mol %), we found that the final step domino reaction proceeded smoothly and gave the desired tetracyclic compound **4a** in 80% yield over two steps starting from **2a**. Switching to other Lewis or Brønsted acids, such as $FeCl_3·6H_2O$, $FeBr_3$, $InCl_3$, AgOTf, $AlCl_3$, $ZnCl_2$, *p*-TsOH, and TfOH, to carry out this transformation under similar conditions proved to be less efficient with respect to time, temperature, and yield (Table 1). Various other solvents such as THF, toluene, and acetonitrile

Scheme 2. Preparation of Intermediate 1-Halo-(2-prop-2-ynyloxy)benzene Derivatives



DOI: 10.1021/acs.joc.5b02637
J. Org. Chem. 2016, 81, 1164–1174

Scheme 3. Two-Step Preparation of Tetracyclic Dibenzofuran 4a

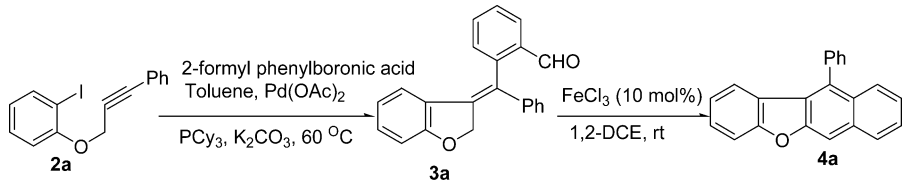
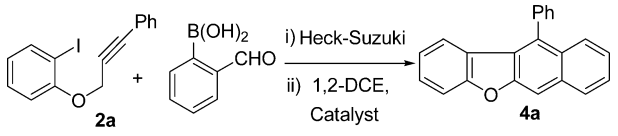


Table 1. Optimization of Reaction Conditions for the Cycloisomerization and Aromatization Process of 3a to 4a[a]



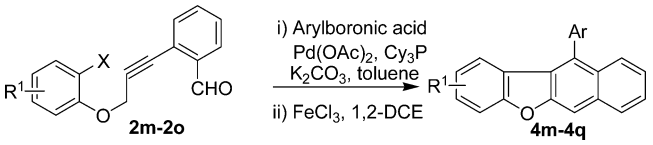
entry	catalyst	temp (°C)	time (h)	yield (%)
1	$FeCl_3$	rt	2	80
2	$FeCl_3{\cdot}6H_2O$	60	1	70
3	$FeBr_3$	60	1	58
4	$InCl_3$	60	1.5	65
5	$In(OTf)_3$	60	4	62
6	AgOTf	60	2	70
7	*p*-TsOH	60	4	65
8	TfOH	60	1	72
9	$AlCl_3$	80	5	35[b]
10	$ZnCl_2$	80	6	20
11	CuCl	80	6	n.r.

[a]Reaction conditions: (i) substrate **2a** (0.5 mmol), 2-formyl phenylboronic acid (0.75 mmol), $Pd(OAc)_2$ (5 mol %), PCy_3(10 mol %), toluene (2 mL), EtOH (2 mL), K_2CO_3(aq) (2.5 M, 2 mL); (ii) catalyst (10 mol %), 1,2-dichloroethane (3 mL). [b]2.5 equiv of $AlCl_3$.

were also studied, but they did not give better results. Thus, anhydrous $FeCl_3$ (10 mol %) in 1,2-dichloroethane was used as the standard reaction conditions in further studies without isolating the intermediate Heck–Suzuki products.

After identifying the best reaction conditions ($FeCl_3$ in 1,2-dichloroethane), we decided to study the scope of this reaction on various substrates with different functional groups with crude Heck–Suzuki products. Both electron-donating groups, such as -Me and -OMe (Scheme 4, entries **4b** and **4g–4j**), and electron-withdrawing groups, such as -Cl and -NO_2, were well-tolerated (Scheme 4, entries **4c** and **4e**) and gave high yields of the desired tetracyclic ring in a two-step process. Interestingly, when dibromo-bearing aryl ethers **2e** were used in the domino Heck–Suzuki coupling reaction, one halide participated in the Heck–Suzuki reaction and the other underwent only a Suzuki reaction with 2-formyl boronic acids, which was subsequently transformed to the highly functionalized desired tetracyclic product **4e** in 60% yield in two steps without affecting the other -CHO group. The alkyne unit bearing alkyl and aryl groups also underwent a smooth conversion to the desired product in high yields. Moreover, a variety of functional groups such as -COMe, -OMe, and -Cl on the aryl ring of the alkyne were also tolerated for Heck–Suzuki coupling and subsequent $FeCl_3$-catalyzed cycloisomerization and dehydration and gave good yields over two steps. It is noteworthy that a 2-thiophenyl unit on the alkyne's terminus also underwent smooth Heck–Suzuki coupling and subsequent cyclization reactions to produce hybrid heterocycle **4h** (Scheme 4) in 63% yield.

Table 2. Domino Synthesis of Polycyclic Dibenzofurans with a Variety of Aryl Boronic Acids



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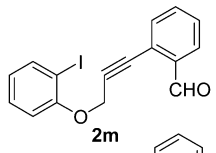
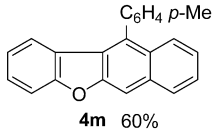
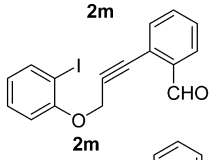
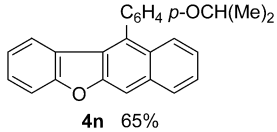
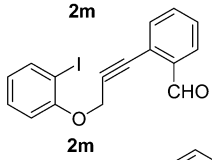
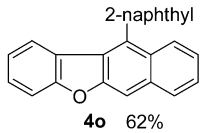
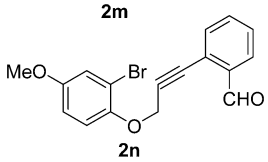
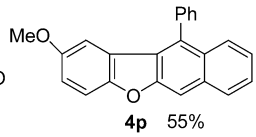
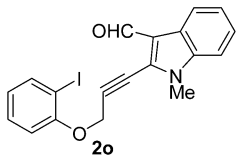
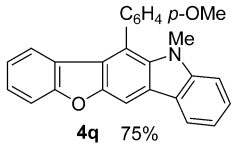
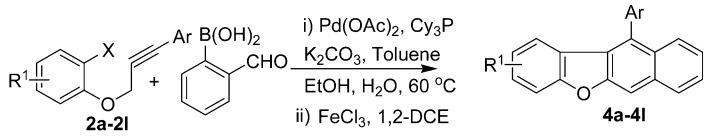
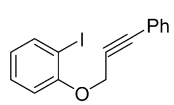
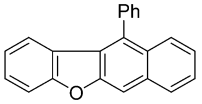
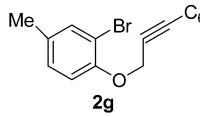
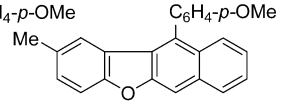
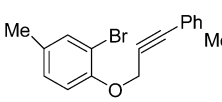
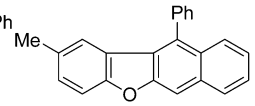
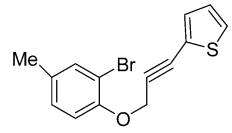
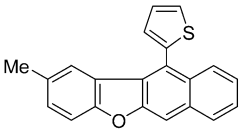
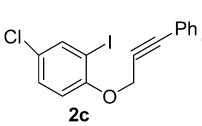
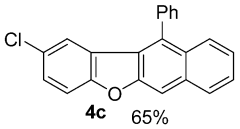
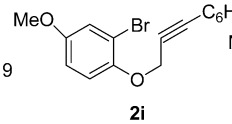
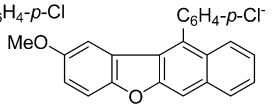
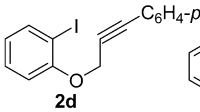
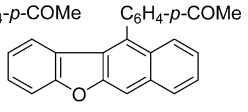
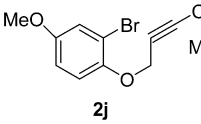
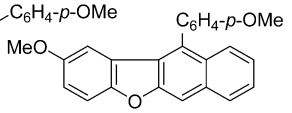
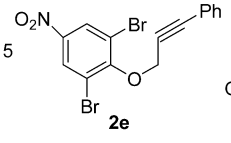
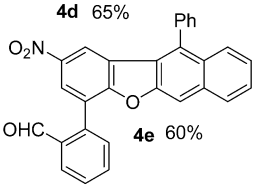
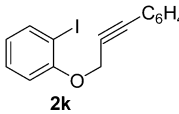
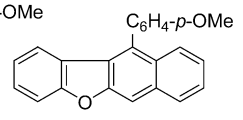
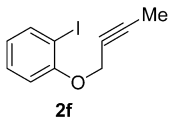
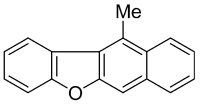
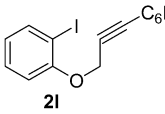
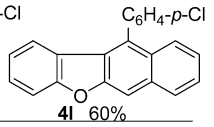
1		
2		
3		
4		
5		

To demonstrate the flexibility of this strategy, we also prepared a series of 2-halo propargyl ethers of 2-formyl benzene **2m–2o** at the alkyne's terminus (Table 2) so that any aryl boronic acid could be utilized for these domino Heck–Suzuki coupling reactions instead of 2-formyl phenyl boronic acid. Gratifyingly, we observed that substrates **2m–2o** also smoothly underwent the two-step domino strategy to form tetracyclic dibenzofuran derivatives **4m–4q** in 60–75% yields (Table 2). For example, 2-naphthyl boronic acid underwent a smooth conversion to produce naphthyl-bearing tetracyclic dibenzofuran ring structure **4o** in 62% overall yield in two steps (Table 2, entry 3). Pleasantly, we also succeeded in synthesizing pentacyclic indole-fused dibenzobenzofuran derivatives **4q** from substrate **2o** via the a two-step domino strategy in very good yields (Table 2, entry 5) at 60 °C. Both indoles and dibenzofurans are present in many biologically active natural products as well as in pharmaceutically important substances; hence, hybrid structure **4q** would be a very interesting pharmaceutical agent.

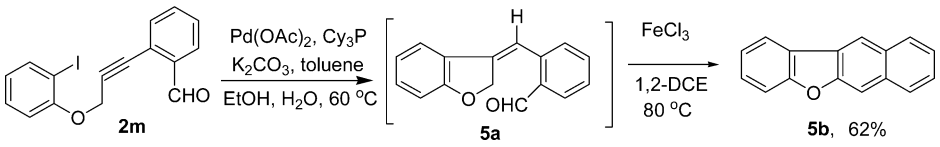
DOI: 10.1021/acs.joc.5b02637
J. Org. Chem. 2016, 81, 1164–1174

Scheme 4. Synthesis of a Variety of Teteracyclic Dibenzofuran Derivatives

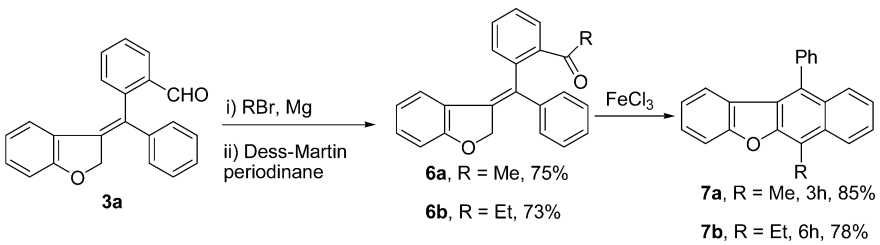


Entry	Substrate	Products	Entry	Substrate	Product
1	 **2a**	 **4a** 80%	7	 **2g**	 **4g** 70%
2	 **2b**	 **4b** 75%	8	 **2h**	 **4h** 63%
3	 **2c**	 **4c** 65%	9	 **2i**	 **4i** 65%
4	 **2d**	 **4d** 65%	10	 **2j**	 **4j** 60%
5	 **2e**	 **4e** 60%	11	 **2k**	 **4k** 85%
6	 **2f**	 **4f** 70%	12	 **2l**	 **4l** 60%

Scheme 5. Strategy for the Synthesis of *β*-Brazan 5b



Scheme 6. Synthesis of Tetracyclic Dibenzofuran Derivatives



Next, we attempted to synthesis the naturally occurring tetracyclic dibenzofuran, *β*-brazan **5b**. The synthesis is depicted in Scheme 5. When substrate **2m** was subjected to carbopalladation and reduction, product **5a** was afforded. Then, the crude product was treated with $FeCl_3$ (10 mol %), providing desired tetracyclic product **5b** in 62% overall yield in two steps. Our approach opens a novel route to the synthesis of this natural product and its derivatives containing substituted tetracyclic dibenzofuran derivatives.

DOI: 10.1021/acs.joc.5b02637
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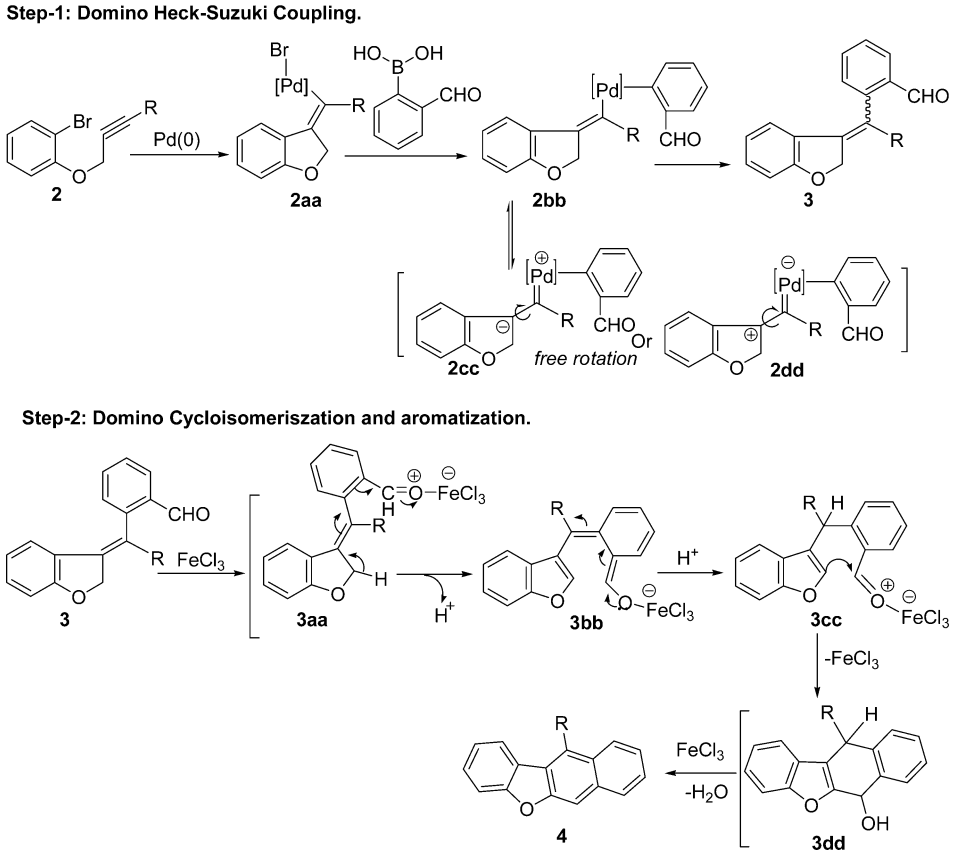
Scheme 7. Plausible Mechanism for the Domino Synthesis of Fused Dibenzofurans



Finally, to make this strategy even more attractive, we also investigated $FeCl_3$-catalyzed cycloisomerization/aromatization of ketones **6a** and **6b**. The strategy is described in Scheme 6. The ketone functional group was introduced in the intermediate of Heck−Suzuki product **3a** by simple two-step reactions. The first step involved reaction of alkyl Grignard reagents with **3a**; then, the intermediate product without isolation was oxidized with Dess−Martin periodinane to obtain **6a** (R = Me) in 75% yield and **6b** (R = Et) in 73% yield. When substrates **6a** and **6b** were treated with $FeCl_3$ (10 mol %) in 1,2-dichloroethane at room temperature, desired products **7a** and **7b** were obtained in 85 and 78% yields, respectively. Thus, this result adds another dimension to the versatility of this strategy.

On the basis of our previous experimental observations and the literature, a plausible reaction pathway is delineated in Scheme 7. In step 1, we propose a mechanism that involves oxidative addition of $Pd(0)/PCy_3$ with 2-halo propargyl ether **2** and is followed by intramolecular *syn*-carbopalladation onto the carbon−carbon triple bond, leading to the generation of alkenylpalladium complex **2aa**. Next, transmetalation between **2aa** and aryl boronic acid in the presence of K_2CO_3 provides intermediate **2bb**, which upon reductive elimination produces product **3** in the syn configuration and regenerates the catalyst for subsequent catalytic cycles. Although the expected product in this sequence is the *syn*-**3** isomer, in many cases we observed the formation of a mixture of syn and anti isomers. Presumably, isomerization of the *syn*-adduct to the anti adduct in the carbopalladation step via zwitterionic intermediate **2cc** or **2dd** and subsequent free rotation around the carbon−carbon σ bond is the major reason for the formation of mixed isomers. This type of isomerization during carbopalladation of an alkyne has also been reported in the literature[10] and in our previous report.[9] For step 2, a preliminary study showed that $FeCl_3$ did not initiate the isomerization/cyclization process of substrate **3** without a 2-formyl group under the employed reaction conditions, even with heating to high temperatures. Therefore, it was concluded that isomerization leading to intermediate **3bb** must be driven by complexation of the carbonyl group of **3** with $FeCl_3$. Then, isomerization as shown in **3aa** and protonation of **3bb** furnished $FeCl_3$-bound intermediate **3cc**, which underwent intramolecular Friedel−Crafts alkylation; subsequent aromatization of **3dd** by dehydration afforded tetracyclic dibenzofuran **3**, which is similar to the mechanism involved in the Bradsher reaction.[11]

CONCLUSIONS

In summary, we have developed a simple and direct approach to access a diverse range of synthetically and biologically important tetracyclic dibenzofuran derivatives by palladium-catalyzed domino carbopalladation/Suzuki coupling and subsequent iron(III)-catalyzed isomerization and cyclodehydration. The strategy was found to be general, to display a wide substrate scope, to have good functional group tolerance, and to provide moderate to high chemical yields. Moreover, this strategy was utilized for the synthesis of naturally occurring β-brazan. Therefore, the present method should be widely applicable in organic and material chemistry.

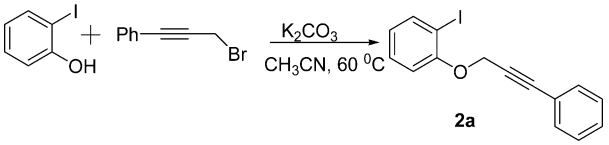
EXPERIMENTAL SECTION

General. ^1H NMR spectra were recorded with a (300, 400 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in

DOI: 10.1021/acs.joc.5b02637
J. Org. Chem. 2016, 81, 1164−1174

parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 7.26) as an internal standard. $^{13}C\{^1H\}$ NMR spectra were recorded with a 300 (75 MHz) or 400 MHz (100 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts of $^{13}C\{^1H\}$ NMR are expressed in parts per million (ppm, δ) and are referenced to $CDCl_3$ (δ = 77.0 ppm) as an internal standard. HRMS measurements were performed by the ESI-TOF method.

Representative Experimental Procedure for the Synthesis of Propargylic Ether (2a).



To a solution of compound 2-iodo phenol (220 mg, 1 mmol) in dry acetonitrile (3 mL) were added phenyl propargyl bromide (213 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol). The resulting mixture was heated at 60 °C for 2 h. After completion of the reaction, the reaction mixture was extracted with dichloromethane. The organic extract was washed with brine solution, dried over anhydrous Na_2SO_4, and concentrated. The crude reaction product was purified by column chromatography using silica gel (60−120 mesh) and eluting with petroleum ether to obtain product **2a** as a colorless viscous liquid (300 mg, 89%). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.00 (s, 2H), 6.75−6.80 (m, 1H), 7.11 (d, J = 8.2 Hz, 1H), 7.33 (s, 4H), 7.45 (s, 2H), 7.81−7.84 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.9, 83.5, 86.4, 87.7, 113.4, 122.2, 123.4, 128.3, 128.8, 129.4, 131.8, 139.7, 156.6 ppm. HRMS (ESI-TOF): calcd for $C_{15}H_{12}IO$ $[M + H]^+$, 334.9933; found, 334.9930.

2-Bromo-4-methyl-1-((3-phenylprop-2-yn-1-yl)oxy)benzene (2b). 4-Methyl 2-bromo phenol (187 mg, 1 mmol) in dry acetonitrile was treated with phenyl propargyl bromide (213 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol), as described for the synthesis **2a**, for 2 h to afford product **2b** as a colorless viscous liquid (250 mg, 0.83 mmol, 83%). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 3H), 4.96 (s, 2H), 7.03−7.07 (m, 2H), 7.27−7.33 (m, 3H), 7.39 (s, 1H), 7.41−7.44 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.2, 58.1, 83.6, 87.6, 112.4, 114.8, 122.3, 128.3, 128.8, 131.8, 132.6, 133.2, 132.6, 133.2, 133.9, 152.2 ppm. HRMS (ESI-TOF): calcd for $C_{16}H_{14}BrO$ $[M + H]^+$, 301.0228; found, 301.0227.

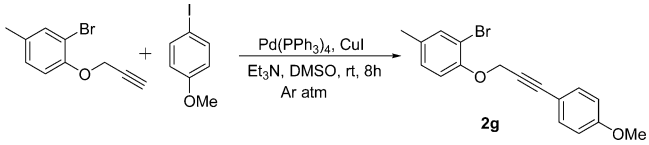
4-Chloro-2-iodo-1-((3-phenylprop-2-yn-1-yl)oxy)benzene (2c). 4-Chloro 2-iodo phenol (255 mg, 1 mmol) in dry acetonitrile was treated with phenyl propargyl bromide (213 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol), as described for the synthesis **2a**, for 2 h to afford product **2c** as a white solid (295 mg, 0.80 mmol, 80%). mp 64 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.96 (s, 2H), 7.01 (d, J = 8.8 Hz, 1H), 7.28−7.33 (m, 4H), 7.39−7.44 (m, 2H), 7.77 (d, J = 1.9 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 58.2, 82.9, 87.0, 88.1, 113.9, 121.9, 127.3, 128.4, 128.9, 129.1, 131.8, 138.8, 139.1, 155.5 ppm. HRMS (ESI-TOF): calcd for $C_{15}H_{11}ClIO$ $[M + H]^+$, 368.9543; found, 368.9542.

1-(4-(3-(2-Iodophenoxy)prop-1-yn-1-yl)phenyl)ethanone (2d). 2-Iodo phenol (220 mg, 1 mmol) in dry acetonitrile was treated with 4-acetyl phenyl propargyl bromide (260 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol), as described for the synthesis **2a**, for 2 h to afford product **2d** as a colorless viscous liquid (320 mg, 0.85 mmol, 85%). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.58 (s, 3H), 5.00 (s, 2H), 6.77−6.79 (m, 1H), 7.07 (dd, J = 1.2, 8.2 Hz, 1H), 7.30−7.34 (m, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.80 (dd, J = 1.6, 7.8 Hz, 1H), 7.88 (dd, J = 1.7, 6.8 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.6, 57.8, 86.7, 86.8, 113.3, 126.9, 128.2, 129.4, 131.9, 136.7, 139.8, 156.5, 197.2 ppm. HRMS (ESI-TOF): calcd for $C_{17}H_{14}IO_2$ $[M + H]^+$, 377.0038; found, 377.0036.

1,3-Dibromo-5-nitro-2-((3-phenylprop-2-yn-1-yl)oxy)-benzene (2e). 4-Nitro 2,6-dibromo phenol (295 mg, 1 mmol) in dry acetonitrile was treated with phenyl propargyl bromide (213 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol), as described for the synthesis **2a**, for 2 h to afford product **2e** as a yellow solid (37 mg, 0.80 mmol, 80%). mp 98 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.15 (s, 2H), 7.27−7.40 (m, 5H), 8.43 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 61.9, 82.2, 89.1, 119.4, 121.7, 127.6, 128.1, 128.3, 128.4, 128.9, 131.6, 144.5, 157.7 ppm. HRMS (ESI-TOF): calcd for $C_{15}H_{10}Br_2NO_3$ $[M + H]^+$, 409.9027; found, 409.9028.

1-(But-2-yn-1-yloxy)-2-iodobenzene (2f). 2-Iodo phenol (220 mg, 1 mmol) in dry acetonitrile was treated with methyl propargyl bromide (163 mg, 1.1 mmol) and dry K_2CO_3 (414 mg, 3 mmol), as described for the synthesis of **2a**, for 2 h to afford product **2f** as a colorless viscous liquid (244 mg, 0.85 mmol, 85%). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.85 (t, J = 2.3 Hz, 3H), 4.71 (q, J = 2.2 Hz, 2H), 6.70−6.76 (m, 1H), 6.99 (dd, J = 1.1, 8.2 Hz, 1H), 7.27−7.33 (m, 1H), 7.77 (dd, J = 1.5, 7.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ3.8, 57.6, 73.7, 84.3, 86.7, 113.1, 123.1, 124.5, 129.4, 139.6, 156.6 ppm. HRMS (ESI-TOF): calcd for $C_{10}H_{10}IO$ $[M + H]^+$, 272.9776; found, 272.9775.

Representative Experimental Procedure for the Synthesis of Propargylic Ether (2g).



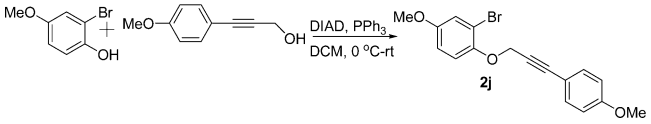
To a solution of 2-bromo-4-methyl-1-(prop-2-yn-1-yloxy)benzene (225 mg, 1.0 mmol), *p*-anisole (257 mg, 1.1 mmol), and triethyl amine (202 mg, 2.0 mmol) in DMSO (5 mL) were added CuI (4 mg, 0.02 equiv) and $Pd(PPh_3)_4$ (12 mg, 0.01 equiv) successively. The resulting mixture was stirred at room temperature for 8 h under an argon atmosphere. After completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc. The organic extract was washed with brine solution, dried over anhydrous Na_2SO_4, and concentrated. The product was subjected to column chromatography (silica gel, 60−120 mesh), eluting with pet. ether/EtOAc 98:2 (v/v) to afford product **2g** as a light yellow viscous liquid (300 mg, 0.9 mmol, 90%). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 3H), 3.80 (s, 3H), 4.94 (s, 2H), 6.81 (d, J = 8.8 Hz, 2H), 7.05−7.09 (m, 2H), 7.36 (d, J = 8.8 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.2, 55.3, 58.2, 82.3, 87.6, 112.3, 113.9, 114.3, 114.7, 128.8, 133.3, 133.9, 152.2, 159.9 ppm. HRMS (ESI-TOF): calcd for $C_{17}H_{16}BrO_2$ $[M + H]^+$, 331.0334; found, 331.0331.

2-(3-(2-Bromo-4-methylphenoxy)prop-1-yn-1-yl)thiophene (2h). Compound 2-bromo-4-methyl-1-(prop-2-yn-1-yloxy)benzene (225 mg, 1.0 mmol) in DMSO was treated with 2-iodo thiophene (230 mg, 1.1 mmol), triethyl amine (202 mg, 2.0 mmol), CuI (4 mg, 0.02 equiv), and $Pd(PPh_3)_4$ (12 mg, 0.01 equiv), as described for the synthesis of **2g**, to afford the **2h** as a light yellow viscous liquid (280 mg, 0.91 mmol, 91%). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 3H), 4.96 (s, 2H), 6.95−6.99 (m, 1H), 7.02 (s, 1H), 7.08 (d, J = 8.5 Hz, 1H), 7.21 (d, J = 3.5 Hz, 1H), 7.25−7.27 (m, 1H), 7.38 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.2, 58.1, 80.9, 87.6, 112.4, 114.8,122.1, 126.9, 127.7, 128.8, 132.7, 132.8, 133.9, 152.1 ppm. HRMS (ESI-TOF): calcd for $C_{14}H_{12}BrOS$ $[M + H]^+$, 306.9792; found, 306.9790.

2-Bromo-1-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)-4-methoxybenzene (2i). 2-Bromo-4-methoxy-1-(prop-2-yn-1-yloxy)-benzene (241 mg, 1.0 mmol) in DMSO was treated with 1-chloro-4-iodobenzene (262 mg, 1.1 mmol) triethyl amine (202 mg, 2.0 mmol), CuI (4 mg, 0.02 equiv), and $Pd(PPh_3)_4$ (12 mg, 0.01 equiv), as described for the synthesis of **2g**, to afford the **2i** as a light yellow viscous liquid (330 mg, 0.94 mmol, 94%). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.78 (s, 3H), 4.93 (s, 2H), 6.85 (dd, J = 2.9, 8.9 Hz, 1H), 7.10 (d, J = 8.9 Hz, 1H), 7.16 (d, J = 2.9 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.8, 58.9, 84.8, 86.4, 113.6, 116.8, 118.9, 120.7, 128.7, 133.0, 134.8, 137.7, 148.5, 155.1 ppm. HRMS (ESI-TOF): calcd for $C_{16}H_{13}BrClO_2$ $[M + H]^+$, 350.9787; found, 350.9785.

DOI: 10.1021/acs.joc.5b02637
J. Org. Chem. 2016, 81, 1164−1174

Representative Experimental Procedure for the Synthesis of Propargylic Ether (2j).



To an ice-cooled solution of 4-methoxy-2-bromo phenol (203 mg, 1.0 mmol), *p*-methoxy phenyl propargyl alcohol (195 mg, 1.2 mmol), and PPh_3 (393 mg, 1.5 mmol) in dry dichloromethane was added a solution of di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol) in dichoromethane under an argon atmosphere. Then, the reaction continued at room temperature for 28 h. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with dichloromethane, dried over anhydrous Na_2SO_4, and concentrated. The crude reaction product was purified by column chromatography using silica gel (60−120 mesh) and eluting with pet. ether to afford product **2j** as a colorless viscous liquid (300 mg, 0.8 mmol, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.76 (s, 3H), 3.80 (s, 3H), 4.91 (s, 2H), 6.81−6.84 (m, 3H), 7.09−7.13 (m, 2H), 7.34−7.40 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.2, 55.8, 59.0, 82.4, 87.6, 113.5, 113.7, 113.9, 114.3, 116.7, 118.8, 133.3, 148.6, 154.9, 159.9 ppm. HRMS (ESI-TOF): calcd for $C_{17}H_{16}BrO_3$ $[M + H]^+$, 347.0283; found, 347.0282.

1-Iodo-2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)benzene (2k). 2-Iodo phenol (220 mg, 1.0 mmol), *p*-methoxy phenyl propargyl alcohol (194 mg, 1.2 mmol), and PPh_3 (393 mg, 1.5 mmol) in dry dichloromethane were treated with di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol), as described for the synthesis of **2j**, for 28 h to afford product **2k** as a colorless viscous liquid (290 mg, 0.8 mmol, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.78 (s, 3H), 4.97 (s, 2H), 6.75 (dt, J = 1.2, 7.6 Hz, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.08−7.11 (m, 1H), 7.30−7.40 (m, 3H), 7.80 (dd, J = 1.5, 7.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.3, 58.0, 82.2, 86.8, 87.7, 113.4, 113.9, 114.2, 123.3, 129.4, 133.4, 139.7, 156.7, 159.9 ppm. HRMS (ESI-TOF): calcd for $C_{16}H_{14}IO_2$ $[M + H]^+$, 365.0038; found, 365.0035.

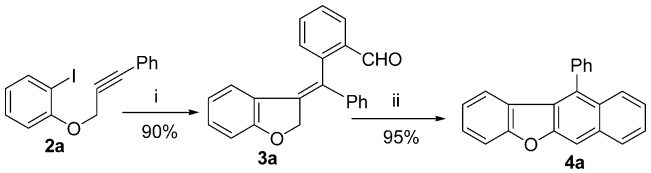
1-((3-(4-Chlorophenyl)prop-2-yn-1-yl)oxy)-2-iodobenzene (2l). 2-Iodo phenol (220 mg, 1.0 mmol), *p*-chloro phenyl propargyl alcohol (200 mg, 1.2 mmol), and PPh_3 (393 mg, 1.5 mmol) in dry DCM were treated with di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol), as described for the synthesis of **2j**, for 24 h to afford product **2l** as a colorless viscous liquid (276 mg, 0.75 mmol, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.97 (s, 2H), 6.76 (dt, J = 1.3, 7.5 Hz, 1H), 7.06 (dd, J = 1.2, 8.2 Hz, 1H), 7.28−7.31 (m, 2H), 7.34−7.37 (m, 3H), 7.81 (dd, J = 1.5, 7.8 Hz, 1H) ppm.^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.8, 84.5, 86.6, 113.4, 120.7, 123.5, 128.7, 129.4, 133.1, 134.9, 139.7, 156.6 ppm. HRMS (ESI-TOF): calcd for $C_{15}H_{11}ClIO$ $[M + H]^+$, 368.9543; found, 368.9541.

2-(3-(2-Iodophenoxy)prop-1-yn-1-yl)benzaldehyde (2m). 2-Iodo phenol (220 mg, 1.0 mmol), 2-(3-hydroxyprop-1-yn-1-yl)-benzaldehyde (192 mg, 1.2 mmol), and PPh_3 (393 mg, 1.5 mmol) in dry DCM were treated with di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol), as described for the synthesis of **2j**, for 20 h to afford product **2m** as a dark yellow viscous liquid (280 mg, 0.77 mmol, 77%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.04 (s, 2H), 6.77 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 9.1 Hz, 1H), 7.31−7.37 (m, 1H), 7.41−7.46 (m, 1H), 7.53 (d, J = 3.7 Hz, 2H), 7.80 (dd, J = 1.4, 7.8 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 10.4 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.7, 83.5, 86.9, 90.5, 113.4, 123.7, 125.4, 127.3, 129.2, 129.4, 133.5, 133.7, 136.3, 139.9, 156.4, 191.2 ppm. HRMS (ESI-TOF): calcd for $C_{16}H_{12}IO_2$ $[M + H]^+$, 362.9882; found, 362.9883.

2-(3-(2-Bromo-4-methoxyphenoxy)prop-1-yn-1-yl)benzaldehyde (2n). 4-Methoxy 2-bromo phenol (203 mg, 1.0 mmol), 2-(3-hydroxyprop-1-yn-1-yl)benzaldehyde (192 mg, 1.2 mmol), and PPh_3 (393 mg, 1.5 mmol) in dry dichloromethane were treated with di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol), as described for the synthesis of **2j**, for 24 h to afford product **2n** as a dark yellow viscous liquid (275 mg, 0.79 mmol, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.79 (s, 3H), 5.02 (s, 2H), 6.86 (dd, J = 2.9, 8.9 Hz, 1H), 7.11 (d, J = 8.9 Hz, 1H), 7.17 (d, J = 2.9 Hz, 1H), 7.44−7.51 (m, 1H), 7.55−7.57 (m, 2H), 7.92 (d, J = 7.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.9, 58.9, 83.3, 90.9, 113.7, 116.9, 119.0, 125.5, 127.3, 128.3, 128.5, 129.1, 133.5, 133.7, 136.2, 148.3, 155.3, 191.3 ppm. HRMS (ESI-TOF): calcd for $C_{17}H_{13}BrNaO_3$ $[M + Na]^+$, 366.9946; found, 366.9945.

2-(3-(2-Iodophenoxy)prop-1-yn-1-yl)-1-methyl-1*H*-indole-3-carbaldehyde (2o). 2-Iodo phenol (220 mg, 1.0 mmol), 2-(3-hydroxyprop-1-yn-1-yl)-1-methyl-1*H*-indole-3-carbaldehyde (255 mg, 1.2 mmol), and PPh_3 (393 mg, 1.5 mmol) in dry dichloromethane were treated with di-isopropyl azo dicarboxylate (303 mg, 1.5 mmol), as described for the synthesis of **2j**, for 24 h to afford product **2o** as a dark yellow viscous liquid (290 mg, 0.70 mmol, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.76 (s, 3H), 5.14 (s, 2H), 6.80 (dt, J = 1.3, 7.6 Hz, 1H), 7.07 (dd, J = 1.3, 8.2 Hz, 1H), 7.30−7.39 (m, 4H), 7.82 (dd, J = 1.5 Hz, 7.8, 1H,), 8.27−8.30 (m, 1H), 10.0 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 31.1, 57.6, 86.9, 95.4, 109.8, 113.4, 120.6, 122.2, 123.4, 123.6, 124.2, 125.3, 129.8, 130.2, 137.4, 139.9, 156.1, 184.9 ppm. HRMS (ESI-TOF): calcd for $C_{19}H_{15}INO_2$ $[M + H]^+$, 416.0147; found, 416.0144.

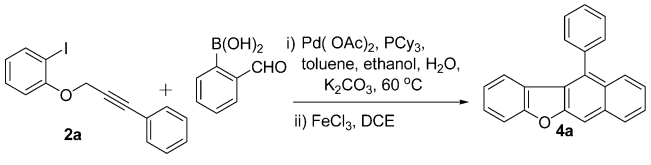
Representative Experimental Procedure for the Two-Step Synthesis of 11-Phenylnaphtho[2,3-*b*]benzofuran (4a).



Synthesis of 3a.[9a] To a solution of **2a** (167 mg, 0.5 mmol) in toluene (2 mL) and ethanol (2 mL) were added K_2CO_3(aq) (2.5 M, 2 mL), PCy_3 (14 mg, 0.05 mmol), and $Pd(OAc)_2$ (6 mg, 0.025 mmol) successively. The resulting solution was stirred at 60 °C under an argon atmosphere for 1 h. After completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc. The organic extract was washed with brine solution, dried over anhydrous Na_2SO_4, and concentrated. After completion of the reaction (monitored by TLC), the solvent was evaporated and the product was purified by column chromatography using silica gel (60−120 mesh), eluting with pet. ether/EtOAc to afford product **3a** as a light green solid (140 mg, 0.45 mmol, 90%). mp 189 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.35−5.49 (m, 2H), 5.89 (d, J = 7.8 Hz, 1H), 6.53 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 7.07−7.12 (m, 1H), 7.19 (d, J = 7.5 Hz, 2H), 7.28−7.39 (m, 4H), 7.57 (t, J = 7.5 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 8.07 (d, J = 7.7 Hz, 1H), 10.16 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 56.8, 75.3, 110.7, 120.7, 124.2, 125.3, 127.6, 127.8, 127.9, 128.4, 128.7, 128.8, 129.0, 130.6, 131.3, 133.7, 134.3, 135.2, 137.1, 141.1, 144.8, 164.3, 192.0 ppm. HRMS (ESI-TOF): calcd for $C_{22}H_{17}O_2$ $[M + H]^+$, 313.1229; found, 313.1228.

Synthesis of 4a.[9a] To a solution of compound **3a** (94 mg, 0.3 mmol) in 1,2-dichloethane was added anhydrous $FeCl_3$ (5 mg, 0.03 mmol) under an argon atmosphere at room temperature for 2 h to afford **4a** as a white solid (84 mg, 0.28 mmol, 95%). mp 102 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.93 (d, J = 7.8 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.37 (m, 2H), 7.51−7.56 (m, 4H), 7.61−7.67 (m, 3H), 7.78 (d, J = 8.5 Hz, 1H), 7.96 (s, 1H), 8.03 (d, J = 8.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 106.4, 111.2, 122.4, 122.8, 123.5, 124.0, 124.2, 125.7, 126.2, 127.8, 128.0, 128.1, 128.9, 129.3, 130.0, 133.1, 134.2, 137.8, 154.2, 157.7 ppm. HRMS: calcd for $C_{22}H_{15}O$ $[M + H]^+$, 295.1123; found, 295.1122. HRMS (ESI-TOF): calcd for $C_{24}H_{17}O_2$ $[M + H]^+$, 295.1123; found, 295.1121.

Representative Experimental Procedure for the Synthesis of 11-Phenylnaphtho[2,3-*b*]benzofuran (4a) without Isolation of 3a.



DOI: 10.1021/acs.joc.5b02637
J. Org. Chem. 2016, 81, 1164−1174

To a solution of **2a** (167 mg, 0.5 mmol) in toluene (2 mL) and ethanol (2 mL) were added 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), PCy_3 (14 mg, 0.05 mmol), and $Pd(OAc)_2$ (6 mg, 0.025 mmol) successively. The resulting solution was stirred at 60 °C under an argon atmosphere for 1 h. After completion of the reaction (monitored by TLC), the crude reaction mixture was extracted with EtOAc. The organic extract was washed with brine solution, dried over anhydrous Na_2SO_4, and concentrated. The crude reaction mixture was dissolved in 1,2-dichloroethane (3 mL), and to this was added $FeCl_3$ (8 mg, 10 mol %). The reaction continued at rt for 2 h under an argon atmosphere. After completion of the reaction (monitored by TLC), the solvent was evaporated and the product was purified by column chromatography using silica gel (60−120 mesh), eluting with pet. ether/EtOAc 98:2 (v/v) to afford product **4a** as a white solid (117 mg, 0.4 mmol, 80%).

2-Methyl-11-phenylnaphtho[2,3-*b*]benzofuran (4b). **2b** (151 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 2 h to afford **4b** as an off-white solid (115 mg, 0.37 mmol, 75%). mp 98 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.27 (s, 3H), 6.68 (s, 1H), 7.21−7.26 (m, 1H), 7.36−7.44 (m, 2H), 7.50−7.55 (m, 3H), 7.63 (d, J = 6.5 Hz, 3H), 7.76 (d, J = 8.5 Hz, 1H) 7.93 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ21.4, 106.4, 110.9, 123.1, 123.7, 124.1, 125.8, 126.4, 127.9, 128.1, 129.0, 129.1, 129.4, 130.1, 131.9, 134.2, 137.9, 154.6, 156.1 ppm. HRMS (ESI-TOF): calcd for $C_{23}H_{17}O$ $[M + H]^+$, 309.1279; found, 309.1276.

2-Chloro-11-phenylnaphtho[2,3-*b*]benzofuran (4c). **2c** (184 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 1 h to afford **4c** as an off-white solid (107 mg, 0.32 mmol, 65%). mp 145 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.81 (d, J = 2.1 Hz, 1H), 7.34−7.56 (m, 6H), 7.63−7.66 (m, 3H), 7.76 (d, J = 8.6 Hz, 1H), 7.94 (s, 1H), 8.01 (d, J = 8.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 106.6, 112.2, 122.6, 124.5, 125.6, 126.4, 127.8, 127.9, 128.5, 129.1, 129.8, 133.4, 134.8, 154.5, 156.0 ppm. HRMS (ESI-TOF): calcd for $C_{22}H_{14}ClO$ $[M + H]^+$, 329.0733; found, 329.0732.

1-(4-(Naphtho[2,3-*b*]benzofuran-11-yl)phenyl)ethanone (4d). **2d** (188 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 2 h to afford **4d** as an off-white solid (108 mg, 0.32 mmol, 65%). mp 148 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.77 (s, 3H), 6.89 (d, J = 7.6 Hz, 1H), 7.04−7.09 (m, 1H), 7.37−7.46 (m, 2H), 7.52−7.68 (m, 2H), 7.63−7.68 (m, 3H), 8.01 (t, J = 8.7 Hz, 2H), 8.24 (d, J = 8.3 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.8, 107.0, 111.4, 122.6, 122.7, 123.3, 123.6, 124.6, 125.8, 125.9, 128.0, 128.4, 128.8, 128.9, 130.1, 132.7, 133.1, 136.9, 143.0, 154.1, 157.8, 197.9 ppm. HRMS (ESI-TOF): calcd for $C_{24}H_{17}O_2$ $[M + H]^+$, 337.1229; found, 337.1228.

2-(2-Nitro-11-phenylnaphtho[2,3-*b*]benzofuran-4-yl)-benzaldehyde (4e). **2e** (206 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (186 mg, 1.25 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 4 h at 60 °C to afford **4e** as a light yellow solid (133 mg, 0.30 mmol, 60%). mp 246 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (dt, J = 0.8, 6.8 Hz, 1H), 7.52−7.60 (m, 4H), 7.69−7.75 (m, 4H), 7.79−7.84 (m, 3H), 7.93 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 8.15−8.18 (m, 1H), 8.37 (d, J = 2.4 Hz, 1H), 9.95 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 107.6, 118.5, 121.8, 122.9, 124.5, 125.3, 126.6, 126.9, 128.1, 129.0, 129.3, 129.5, 129.6, 129.7, 131.5, 133.8, 134.1, 134.2, 135.9, 136.4, 136.9, 143.8, 154.6, 158.3, 190.7 ppm. HRMS (ESI-TOF): calcd for $C_{29}H_{18}NO_4$ $[M + H]^+$, 444.1236; found, 444.1233.

11-Methylnaphtho[2,3-*b*]benzofuran (4f). **2f** (136 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 8 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 2 h at room tempetature to afford **4f** as a white solid (81 mg, 0.35 mmol, 70%). mp 107 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.12 (s, 3H), 7.35−7.41 (m, 1H), 7.48−7.59 (m, 4H), 7.77 (s, 1H), 7.94−7.97 (m, 1H), 8.19−8.25 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.1, 104.9, 111.3, 122.6, 123.3, 123.6, 123.9, 124.0, 124.1, 124.8, 125.6, 127.6, 128.4, 129.2, 129.5, 133.2, 154.3, 157.5 ppm. HRMS (ESI-TOF): calcd for $C_{17}H_{13}O$ $[M + H]^+$, 233.0966; found, 233.0965.

11-(4-Methoxyphenyl)-2-methylnaphtho[2,3-*b*]benzofuran (4g). **2g** (165 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 2 h at 60 °C to afford **4g** as a white solid (118 mg, 0.35 mmol, 70%). mp 135 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.30 (s, 3H), 3.99 (s, 3H), 6.81 (s, 1H), 7.16−7.21 (m, 2H), 7.25 (d, J = 4.9 Hz, 1H), 7.35−7.45 (m, 4H), 7.49 (m, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.91 (s, 1H), 7.99 (d, J = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.4, 55.5, 106.2, 110.7, 114.3, 122.9, 123.8, 124.0, 124.1, 125.6, 126.3, 127.8, 128.9, 129.9, 131.2, 131.8, 133.1, 154.6, 156.0, 159.5 ppm. HRMS (ESI-TOF): calcd for $C_{24}H_{18}NaO_2$ $[M + Na]^+$, 361.1204; found, 361.1205.

2-Methyl-11-(thiophen-2-yl)naphtho[2,3-*b*]benzofuran (4h). **2h** (154 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 1.5 h at room temperature to afford **4h** as a colorless viscous liquid (99 mg, 0.31 mmol, 63%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.35 (s, 3H), 7.03 (s, 1H), 7.23 (t, J = 8.6 Hz, 1H), 7.39−7.44 (m, 1H), 7.46−7.51 (m, 3H), 7.56 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 8.6 Hz, 1H), 7.96 (s, 1H), 8.07 (d, J = 8.3 Hz, 1H), 8.41 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.3, 111.3, 118.8, 120.9, 122.2, 122.6, 123.9, 124.9, 125.3, 126.2, 127.6, 128.7, 129.6, 131.5, 132.5, 138.4, 140.7, 144.2, 153.9 ppm. HRMS (ESI-TOF): calcd for $C_{21}H_{15}OS$ $[M + H]^+$, 315.0844; found, 315.0843.

11-(4-Chlorophenyl)-2-methoxynaphtho[2,3-*b*]benzofuran (4i). **2i** (175 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 8 h at 60 °C to afford **4i** as a white solid (116 mg, 0.32 mmol, 65%). mp 85 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.68 (s, 3H), 6.44 (d, J = 2.4 Hz, 1H), 7.03 (dd, J = 2.5, 8.9 Hz, 1H), 7.39−7.49 (m, 4H), 7.53−7.58 (m, 1H), 7.65 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.4 Hz, 1H), 7.94 (s, 1H), 8.02 (d, J = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.6, 106.5, 106.8, 111.7, 115.5, 123.8, 124.2, 124.4, 125.8, 127.9, 128.9, 129.1, 131.7, 132.5, 133.1, 134.3, 136.1,

DOI: 10.1021/acs.joc.5b02637
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152.4, 154.8, 155.4 ppm. HRMS (ESI-TOF): calcd for $C_{23}H_{16}ClO_2$ $[M + H]^+$, 359.0839; found, 359.0840.

2-Methoxy-11-(4-methoxyphenyl)naphtho[2,3-*b*]-benzofuran (4j). **2j** (174 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 3 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 1 h at 60 °C to afford **4j** as a white solid (106 mg, 0.30 mmol, 60%). mp 104 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.64 (s, 3H), 3.96 (s, 3H), 6.49 (d, J = 2.5 Hz, 1H), 6.99 (dd, J = 2.6, 8.8 Hz, 1H), 7.17 (d, J = 8.6 Hz, 2H), 7.35−7.45 (m, 4H), 7.49−7.54 (m, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.90 (s, 1H), 7.99 (d, J = 8.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.4, 55.6, 106.2, 106.7, 106.7, 111.4, 114.2, 115.2, 124.0, 124.1, 125.6, 126.2, 127.8, 129.4, 129.7, 131.3, 133.2, 133.9, 152.3, 154.9, 155.2, 159.5 ppm. HRMS (ESI-TOF): calcd for $C_{24}H_{19}O_3$ $[M + H]^+$, 355.1334; found, 355.1331.

11-(4-Methoxyphenyl)naphtho[2,3-*b*]benzofuran (4k). **2k** (182 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 1 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 2 h at room temperature to afford **4k** as a white solid (138 mg, 0.43 mmol, 85%). mp 128 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.99 (s, 3H), 7.01 (d, J = 7.7 Hz, 1H), 7.08 (m, 1H), 7.17 (d, J = 8.5 Hz, 2H), 7.36−7.45 (m, 4H), 7.50−7.55 (m, 2H), 7.80 (d, J = 8.5 Hz, 1H), 7.94 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.4, 106.2, 111.2, 114.3, 122.4, 122.9, 123.8, 124.2, 125.7, 125.7, 126.3, 127.8, 127.9, 129.7, 129.9, 1312.2, 133.2, 134.0, 154.2, 157.7, 159.5 ppm. HRMS (ESI-TOF): calcd for $C_{23}H_{16}NaO_2$ $[M + Na]^+$, 347.1048; found, 347.1049.

11-(4-Chlorophenyl)naphtho[2,3-*b*]benzofuran (4l). **2l** (184 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 2 h at room temperature to afford **4l** as a white solid (98 mg, 0.30 mmol, 60%). mp 190 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.97 (d, J = 7.8 Hz, 1H), 7.08−7.13 (m, 1H), 7.37−7.47 (m, 4H), 7.53 (t, J = 7.8 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.5 Hz, 1H), 7.96 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 106.8, 111.4, 122.5, 122.7, 123.6, 123.7, 124.5, 125.8, 127.9, 128.3, 129.1, 129.3, 131.5, 132.6, 133.1, 134.2, 136.2, 154.1, 157.7 ppm. HRMS (ESI-TOF): calcd for $C_{22}H_{14}ClO$ $[M + H]^+$, 329.0733; found, 329.0734.

11-(*para*-Tolyl)naphtho[2,3-*b*]benzofuran (4m). **2m** (181 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 1 h at 60 °C to afford **4m** as a white solid (92 mg, 0.30 mmol, 60%). mp 144 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.57 (s, 3H), 6.98 (d, J = 7.7 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 7.35−7.46 (m, 6H), 7.52 (t, J = 7.8 Hz, 2H), 7.79 (d, J = 8.5 Hz, 1H), 7.94 (s, 1H), 8.01 (d, J = 8.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.5, 106.2, 11.2, 122.4, 122.9, 123.6, 124.1, 124.2, 125.7, 126.4, 127.8, 127.9, 1 29.5, 129.6, 129.9, 133.2, 134.4, 134.7, 137.8, 154.2, 157.7 ppm. HRMS (ESI-TOF): calcd for $C_{23}H_{17}O$ $[M + H]^+$, 309.1279; found, 309.1280.

11-(4-Isopropoxyphenyl)naphtho[2,3-*b*]benzofuran (4n). **2m** (181 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 1.5 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 1 h at room temperature to afford **4n** as a white solid (115 mg, 0.32 mmol, 65%). mp 116 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.48 (d, J = 6.0 Hz, 6H), 4.71−4.77 (m, 1H), 7.05−7.09 (m, 2H), 7.14 (d, J = 8.6 Hz, 2H), 7.39−7.44 (m, 4H), 7.49−7.55 (m, 2H), 7.82 (d, J = 8.5 Hz, 1H), 7.93 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ22.2, 70.1, 106.2, 111.2, 111.6, 116.2, 121.3, 122.4, 123.8, 124.1, 124.2, 125.7, 126.4, 127.8, 127.9, 128.4, 129.6, 129.7, 131.2, 133.2, 134.2, 154.2, 157.7, 157.8 ppm. HRMS (ESI-TOF): calcd for $C_{25}H_{21}O_2$ $[M + H]^+$, 353.1542; found, 353.1540.

11-(Naphthalen-2-yl)naphtho[2,3-*b*]benzofuran (4o). **2m** (181 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 1.5 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 2 h at room temperature to afford **4o** as a white solid (107 mg, 0.31 mmol, 62%). mp 140 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.90 (d, J = 7.7 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 7.38−7.43 (m,2H), 7.53−7.57 (m, 2H), 7.61−7.67 (m, 3H), 7.81 (d, J = 8.6 Hz, 1H), 7.94 (d, J = 7.4 Hz, 1H), 8.01−8.07 (m, 4H), 8.13 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 106.6, 111.3, 122.5, 122.9, 123.7, 124.0, 124.3, 125.8, 126.3, 127.9, 128.0, 128.1, 128.2, 128.7, 129.1, 129.5, 133.1, 133.2, 133.7, 134.0, 135.3, 154.3, 157.8 ppm. HRMS (ESI-TOF): calcd for $C_{26}H_{17}O$ $[M + H]^+$, 345.1279; found, 345.1276.

2-Methoxy-11-phenylnaphtho[2,3-*b*]benzofuran (4p). **2n** (172 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 2 h at room temperature to afford **4p** as a white solid (89 mg, 0.27 mmol, 55%). mp 96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.61 (s, 3H), 6.37 (d, J = 2.5, 1H), 7.01 (dd, J = 2.7, 8.9 Hz, 1H), 7.38−7.46 (m, 2H), 7.52−7.58 (m, 3H), 7.61−7.69 (m, 3H), 7.80 (d, J = 8.5 Hz, 1H), 7.94 (s, 1H), 8.03 (d, J = 8.2 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.5, 106.3, 106.4, 111.5, 115.6, 124.2, 124.5, 125.7, 126.2, 127.8, 128.1, 128.9, 130.2, 133.2, 134.1, 137.7, 152.4, 154.9, 155.3 ppm. HRMS (ESI-TOF): calcd for $C_{23}H_{17}O_2$ $[M + H]^+$, 325.1229; found, 325.1228.

2-Methoxy-12-(4-methoxyphenyl)-11-methyl-11*H*-benzofuro[3,2-*b*]carbazole (4q). **2o** (207 mg, 0.5 mmol) in toluene and ethanol was treated with 2-formyl phenyl boronic acid (112 mg, 0.75 mmol), K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 2 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the synthesis of **4a**, for 3 h at 60 °C to afford **4q** as an off-white solid (153 mg, 0.38 mmol, 75%). mp 178 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.39 (s, 3H), 3.98 (s, 3H), 6.79 (d, J = 7.7 Hz, 1H), 7.01−7.06 (m, 1H), 7.10−7.13 (m, 2H), 7.23−7.28 (m, 1H), 7.31−7.38 (m, 2H), 7.46−7.55 (m, 4H), 8.16−8.20 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 32.3, 55.4, 100.8, 108.6, 111.2, 114.0, 118.6, 118.7, 120.2, 121.9, 122.0, 122.6, 122.8, 123.8, 125.2, 126.2, 126.4, 129.4, 131.6, 135.6, 143.0, 150.4, 157.1, 159.6 ppm. HRMS (ESI-TOF): calcd for $C_{26}H_{20}NO_2$ $[M + H]^+$, 378.1494; found, 378.1492.

Naphtho[2,3-*b*]benzofuran (5b).[12] **2m** (181 mg, 0.5 mmol) in toluene and ethanol was treated with K_2CO_3(aq) (2.5 M, 2 mL), $Pd(OAc)_2$ (6 mg, 0.025 mmol), and PCy_3 (14 mg, 0.05 mmol), as described for the Suzuki step for the synthesis of **4a**, for 1.5 h; then, $FeCl_3$ (8 mg, 10 mol %) was added to the crude reaction mixture in 1,2-dichloroethane, as described for the cyclization step for the

DOI: 10.1021/acs.joc.5b02637
J. Org. Chem. 2016, 81, 1164−1174

synthesis of **4a**, for 1 h at 80 °C to afford **5b** as a white solid (77 mg, 0.31 mmol, 62%). mp 205 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35−7.40 (m, 1H), 7.46−7.59 (m, 4H), 7.92 (s, 1H), 7.97 (d, J = 7.83, 1H), 8.02−8.08 (m, 2H), 8.41 (s, 1H) ppm. HRMS (ESI-TOF): calcd for $C_{16}H_{11}O$ $[M + H]^+$, 219.0810; found, 219.0808.

General Representative Procedure for the Synthesis of (*E*)-1-(2-(Benzofuran-3(2*H*)-ylidene(phenyl)methyl)phenyl)-ethanone (6a). Mg (18 mg, 0.75 mmol) was taken in a two-necked round-bottomed flask and heated with a spirit lamp for 15 min. Then, one granule of iodine was added to it, and it was heated on an oil bath at 140 °C for 15 min and cooled to room temperature. Methyl iodide (106 mg, 0.75 mmol) in diethyl ether (5 mL) was added to the activated Mg, and the mixture was refluxed for 30 min and cooled to room temperature. Then, **3a** (156 mg, 0.5 mmol) in diethyl ether (5 mL) was added, and the reaction was continued at room temperature for 30 min. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with NH_4Cl(aq), extracted with diethyl ether, dried over anhydrous Na_2SO_4, and concentrated. The crude alcohol was dissolved in dichloromethane (5 mL), and Dess−Martin periodinane (318 mg, 0.75 mmol) was added. The reaction was continued at room temperature for 30 min. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with dichloromethane, dried over anhydrous Na_2SO_4, and concentrated. The crude reaction mixture was purified by column chromatography using silica gel (60−120 mesh) to afford product **6a** as a green viscous liquid (122 mg, 0.37 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34 (s, 3H), 5.33 (d, J = 14.8 Hz, 1H), 5.50 (d, J = 14.8 Hz, 1H), 6.56−6.61 (m, 1H), 6.87 (d, J = 8.1 Hz, 1H), 7.08−7.14 (m, 1H), 7.22−7.28 (m, 3H), 7.33−7.41 (m, 4H), 7.50−7.62 (m, 2H), 7.82 (dd, J = 1.3, 7.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.0, 75.4, 110.4, 120.3, 124.1, 125.9, 127.3, 128.0, 128.2, 128.3, 129.4, 129.9, 131.6, 131.8, 132.3, 133.9, 139.4, 140.2, 140.9, 164.0, 200.6 ppm. HRMS (ESI-TOF): calcd for $C_{23}H_{19}O_2$ $[M + H]^+$, 327.1385; found, 327.1386.

(*E*)-1-(2-(Benzofuran-3(2*H*)-ylidene(phenyl)methyl)phenyl)-propan-1-one (6b). Mg (18 mg, 0.75 mmol) was taken in a two-necked round-bottomed flask and heated with a spirit lamp for 15 min. Then, one granule of iodine was added to it, and it was heated on an oil bath at 140 °C for 15 min and cooled to room temperature. Ethyl bromide (81 mg, 0.75 mmol) in THF (5 mL) was added to the activated Mg, and the mixture was stirred at room temperature until a color change took place. Then, **3a** (156 mg, 0.5 mmol) in THF (5 mL) was added, and the reaction was continued at room temperature for 30 min. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with NH_4Cl(aq), extracted with diethyl ether, dried over anhydrous Na_2SO_4, and concentrated. The crude alcohol was dissolved in DCM (5 mL), and Dess−Martin periodinane (318 mg, 0.75 mmol) was added. The reaction was continued at room temperature for 30 min. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with DCM, dried over anhydrous Na_2SO_4, and concentrated. The crude reaction mixture was purified by column chromatography using silica gel (60−120 mesh) to afford product **6b** as a green viscous liquid (124 mg, 0.36 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.78−0.88 (m, 3H), 2.58−2.69 (m, 2H), 5.27 (d, J = 14.7 Hz, 1H), 5.45 (d, J = 14.7 Hz, 1H), 6.11 (d, J = 7.7 Hz, 1H), 6.57−6.62 (m, 1H), 6.83 (d, J = 8.0 Hz, 1H), 7.05−7.11 (m, 1H), 7.18−7.40 (m, 5H), 7.48−7.55 (m, 3H), 7.71 (d, J = 7.3, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 8.10, 34.4, 110.4, 120.3, 124.2, 125.9, 127.3, 127.9, 128.3, 128.6, 128.8, 129.9, 131.6, 131.7, 133.9, 139.9, 141.0, 164.0, 204.1 ppm. HRMS (ESI-TOF): calcd for $C_{24}H_{21}O_2$ $[M + H]^+$, 341.1542; found, 341.1543.

Representative Experimental Procedure for the Synthesis of 6-Methyl-11-phenylnaphtho[2,3-*b*]benzofuran (7a). To a solution of **6a** (98 mg, 0.3 mmol) in dry 1,2-dichloroethane (3 mL) was added anhydrous $FeCl_3$ (5 mg, 10 mol %), and the reaction was continued at room temperature for 3 h under an argon atmosphere. After completion of the reaction (monitored by TLC), the solvent was evaporated and the crude reaction mixture was purified by column chromatography using silica gel (60−120 mesh), eluting with pet. ether/EtOAc to obtain product **7a** as a white solid (78 mg, 0.25 mmol, 85%). mp 176 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.97 (s, 3H), 6.90 (d, J = 7.4 Hz, 1H), 7.03−7.08 (m, 1H), 7.39−7.44 (m, 2H), 7.49−7.55 (m, 2H), 7.56−7.64 (m, 5H), 7.79 (d, J = 8.5, 1H), 8.19 (d, J = 8.5 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.2, 111.2, 113.7, 122.3, 122.8, 122.9, 13.6, 123.8, 124.6, 125.4, 126.8, 127.9, 128.0, 128.9, 129.4, 130.3, 131.8, 132.1, 138.1, 15.4, 157.6 ppm. HRMS (ESI-TOF): calcd for $C_{23}H_{17}O$ $[M + H]^+$, 309.1279; found, 309.1277.

6-Ethyl-11-phenylnaphtho[2,3-*b*]benzofuran (7b). **6b** (102 mg, 0.3 mmol) in dry 1,2-dichloroethane was treated with $FeCl_3$ (5 mg, 10 mol %) at room temperature for 6 h to obtain product **7b** as a white solid (75 mg, 0.23 mmol, 78%). mp 96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.52 (t, J = 7.5 Hz, 3H), 3.54 (q, J = 7.5 Hz, 2H), 6.91 (d, J = 7.6 Hz, 1H), 7.04−7.09 (m, 1H), 7.38−7.45 (m, 2H), 7.51−7.54 (m, 2H), 7.57−7.68 (m, 5H), 7.82 (d, J = 8.5 Hz, 1H), 8.25 (d, J = 8.5 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.8, 19.1, 111.2, 120.2, 122.3, 122.8, 122.9, 123.5, 123.7, 124.6, 125.4, 127.0, 127.9, 128.0, 128.9, 129.7, 130.3, 131.2, 131.9, 138.2, 151.9, 157.6 ppm. HRMS (ESI-TOF): calcd for $C_{24}H_{19}O$ $[M + H]^+$, 323.1436; found, 323.1435.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02637.

Crystallographic data for **4a** (CIF)

^{1}H and ^{13}C NMR spectra of compounds **2a−2o**, **3a**, **4a−4q**, **6a−6b**, and **7a−7b**; ^{1}H NMR spectra of **5b**; and X-ray crystal structure of **4a** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jumasish2004@yahoo.co.in or umasishjana@gmail.com. Fax: +91-33-2414-6584.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

K.P. and S.J. are thankful to CSIR, New Delhi, India, for their fellowships. S.K. is thankful to UGC, India, for his fellowship. The X-ray diffractometer facility under the DST-FIST program of the Department of Chemistry (JU) is also gratefully acknowledged.

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